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(Commemoration Issue Dedicated to
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Intermolecular Forces and Stable Configuration of Crystalline Benzoic Acid

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The energy difference between the two configurations of crystalline benzoic acid, which would be transformed into each other by the simultaneous proton transfer along two hydrogen bonds of the dimer, was evaluated by using the empirical atom-atom potentials. This calculation gives reasonable value as compared with the experimental value obtained from infrared spectroscopy, providing the useful information about the stability of the two molecular configurations. It is also apparent that the intermolecular Coulombic force plays an important role in the determination of the stable configuration.

INTRODUCTION

We have previously investigated the temperature dependence of the infrared spectra of crystalline benzoic acid down to liquid helium temperature.¹⁻³⁾ The conclusions are as follows: (1) The *A* and *B* configurations shown in Fig. 1 coexist in the crystal, giving different spectra from each other. (2) The energy difference between them is about 0.1 kcal/mol. (3) There is only one stable configuration at 0°K, and it is probably assigned to the *A* configuration as deduced from the result of the X-ray analysis.⁴⁾ (4) The fact that the two CO bonds in benzoic acid have the nearly equal lengths 1.29 and 1.24 Å at room temperature⁴⁾ can be interpreted as the average values of the C-O and C=O bond lengths of the *A* and *B* configurations.

These results have stimulated us to inquire why the *A* configuration is more stable than the *B* configuration, or where the energy difference between the two configurations arises from. In order to give answers for these questions, we have calculated the energy difference between the *A* and *B* configurations by using the atom-atom potentials such as those of Williams⁵⁾ under the following assumptions: (1) Although the real crystal may randomly contain the *A* and *B* configurations except at 0°K, we consider here the two ideal crystal structures, *A* and *B*, which consist only of the *A* and *B* configurations, respectively, as shown in Fig. 1. (2) The energy difference between the *A* and *B* crystal structure arises from the difference in intermolecular force between the two crystal structures. (3) We approximate the energy difference between the two configurations by that between the two crystal structures.

PROCEDURE FOR CALCULATION

Molecular Model

As we have postulated that the molecular structure obtained for benzoic acid by the

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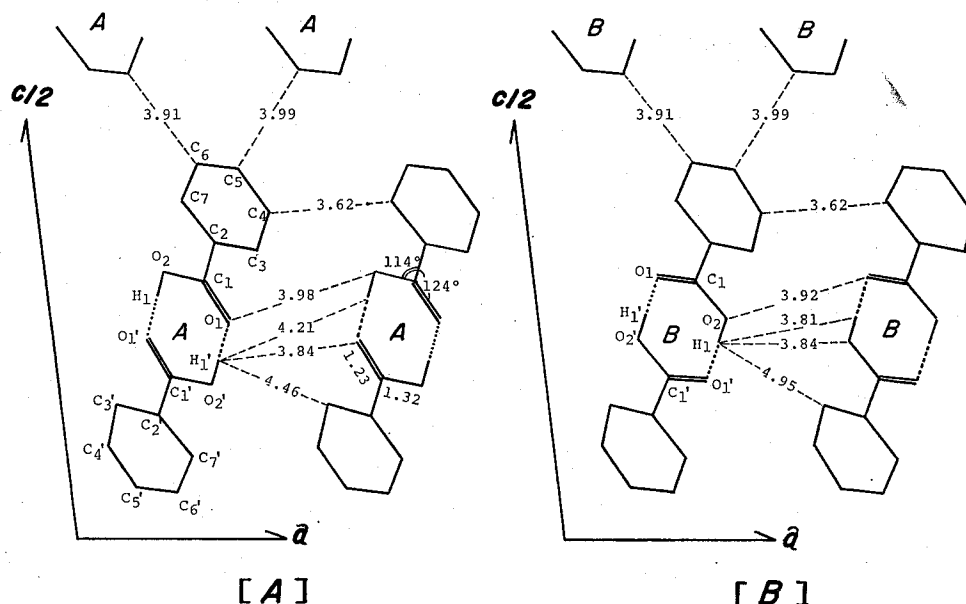


Fig. 1. Models of the two ideal crystal structures of benzoic acid projected upon the ac plane: [A] crystal structure consisting only of the A molecular configurations (C-O bonds nearly parallel to the a -axis); [B] that consisting only of the B configurations (C=O bonds nearly parallel to the a -axis).

X-ray analysis⁴⁾ is the average of the A and B configurations, it is necessary to assume the molecular structures for both A and B configurations. The molecular model of the A configuration is assumed as follows: (1) The coordinates of the carbon atoms C₁, C₂, ..., C₇ are the same as those obtained from the X-ray analysis.⁴⁾ (2) The coordinates of the O₁ and O₂ atoms are calculated by using the usual C—O and C=O bond lengths (1.32 and 1.23 Å, respectively) and C₂C₁O₁ and C₂C₁O₂ angles (124° and 114°, respectively) found in monocarboxylic acids.^{6,7)} (3) The benzene hydrogens are placed radially at a distance of 1.02 Å^{5,8)} from the carbon atoms. (4) The carboxylic hydrogen is placed on

Table I. Coordinates of Atoms in the A and B Configurations

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
A	H ₁	-0.132	-0.001	$A \text{ \& } B$	C ₂	0.180	0.481
	O ₁	0.206	0.239		C ₃	0.383	0.631
	O ₂	-0.088	0.141		C ₄	0.455	0.823
	C ₁	0.103	0.278		C ₅	0.330	0.875
B	H ₁	0.169	0.110		C ₆	0.133	0.720
	O ₁	-0.083	0.132		C ₇	0.051	0.516
	O ₂	0.221	0.255		H ₃	0.470	0.595
	C ₁	0.093	0.274	H ₄	0.602	0.941	
			H ₅	0.391	1.014		
			H ₆	0.035	0.751		
			H ₇	-0.098	0.405		

a line connecting the O₂ and O₁' atoms at a distance of 0.99 Å⁹⁾ from the O₂ atom. The coordinates of atoms thus determined are given in Table I.

The molecular model of the *B* configuration is assumed as follows: (1) The coordinates of the carbon and hydrogen atoms in the benzene ring, C₂-C₇, and H₂-H₇, are the same as in the *A* configuration. (2) The C₁, O₁, O₂, and H₁ atoms are placed at the mirror images of the corresponding atoms of the *A* configuration with respect to the *xz* plane (the *x* axis lies on a line connecting the C₂ and C₂' atoms and the *z*-axis is the normal to the plane formed by the atoms C₁, O₁, and O₂). These coordinates are also given in Table I. The coordinates of the pair of the dimer and of the surrounding molecules were calculated under the assumption of the space group *P*2₁/*c*.⁴⁾

Atom-Atom Potentials and their Parameters

In order to express the atom-atom potential, the equation

$$V_1(r_{ij}) = A \exp(-Br_{ij}) / r_{ij}^D - C / r_{ij}^6 \quad (1)$$

was used, where r_{ij} is the distance between atoms *i* and *j*. The potential $V_1(r_{ij})$ is of the Lennard-Jones type when $B=0$, and it is of the Buckingham type when $D=0$. The sets of parameters used in this paper are listed in Table II. Set I is of the Lennard-Jones 6-12 type and others are of the Buckingham type.

In Set I, the parameters for carbon, hydrogen, and oxygen atoms were approximated by those for neon, helium, and neon atoms, respectively, determined from second virial coefficients of gases.¹⁰⁾ The combining laws for parameters between the unlike atoms, He-Ne, were used.¹¹⁾

In Sets II-IV, the parameters for carbon and hydrogen atoms were those of Williams (Parameter Set IV of Ref. 5) derived from the crystal studies. The values of parameters previously obtained for the oxygen atom are greatly different from one another. We have chosen three parameters¹²⁻¹⁴⁾ as representatives and these are the O-O parameters in Sets II-IV. For the parameters between oxygen and hydrogen, the relations,¹⁵⁾ $A_{OH} =$

Table II. Potential Parameters*

Atom pair	Param. set	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	Atom pair	Param. set	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
C-C	I	52704	0.00	122.1	12	C-H	I	18391	0.00	52.8	12
	II	83630	3.60	568.0	0		II	8766	3.67	125.0	0
	III	83630	3.60	568.0	0		III	8766	3.67	125.0	0
	IV	83630	3.60	568.0	0		IV	8766	3.67	125.0	0
H-H	I	6317	0.00	22.7	12	O-O	I	52704	0.00	122.1	12
	II	2654	3.74	27.3	0		II	30100	4.33	102.1	0
	III	2654	3.74	27.3	0		III	186400	4.55	200.0	0
	IV	2654	3.74	27.3	0		IV	96500	4.33	354.0	0
C-O	I	52704	0.00	122.1	12	O-H	I	18391	0.00	52.8	12
	II	50170	3.97	240.8	0		II	8938	4.04	52.8	0
	III	124900	4.08	337.0	0		III	22240	4.15	73.9	0
	IV	89830	3.97	448.4	0		IV	16000	4.04	98.3	0

* *A* in kcal/mol, *B* in Å⁻¹, *C* in (kcal/mol)·Å⁶.

Table III. Residual (Effective) Charges on Atoms (in electrons)

Atom	Charge	Atom	Charge
H ₁	0.174	O ₁	-0.285
C ₁	0.370	O ₂	-0.259

$(A_{OO}A_{HH})^{1/2}$, $C_{OH}=(C_{OO}C_{HH})^{1/2}$ and $B_{OH}=(B_{OO}+B_{HH})/2$, were assumed. The situation was the same for the parameters between oxygen and carbon atoms.

Coulombic Energy

Besides $V_1(r_{ij})$ which is the atom-atom potential for neutral atoms, the Coulombic energy^{16,17)} between residual charges at atom centers was evaluated as

$$V_2(r_{ij})=e_i e_j / r_{ij}, \quad (2)$$

where e_i and e_j are the residual (effective) charges on atoms i and j , respectively. Residual charges on the atoms C₁, O₁, O₂, and H₁ of the carboxyl group were assumed as in Table III, on the basis of the result of CNDO/2 calculation made for formic acid monomer.¹⁸⁾ It has been reported that the residual charges on each atom of the monomer remains nearly the same when the dimer is formed.¹⁹⁾ Residual charges on other atoms not listed in Table III were assumed to be zero. The final atom-atom potential is the sum of $V_1(r_{ij})$ and $V_2(r_{ij})$;

$$V(r_{ij})=V_1(r_{ij})+V_2(r_{ij}). \quad (3)$$

Enthalpy Difference

Enthalpy difference between the A and B crystal structures can be considered as the sum of the intramolecular and intermolecular part,

$$\Delta H_{\text{total}}=\Delta H_{\text{intra}}+\Delta H_{\text{inter}}. \quad (4)$$

The intramolecular part ΔH_{intra} is calculated as follows (the physical meaning of ΔH_{intra} will be discussed later);

$$\Delta H_{\text{intra}}=H_{\text{intra}}^A-H_{\text{intra}}^B=(1/2) \sum_i \sum_{j \neq i} [V^A(r_{ij})-V^B(r_{ij})]. \quad (5)$$

Here the atoms i and j are within the dimer molecule. (Note that the dimer is treated as one molecular unit.) On the other hand, the intermolecular part ΔH_{inter} is obtained as

$$\Delta H_{\text{inter}}=H_{\text{inter}}^A-H_{\text{inter}}^B=\sum_i \sum_j [V^A(r_{ij})-V^B(r_{ij})], \quad (6)$$

where the atom i is of a certain dimer and the atom j is of surrounding dimers. As the coordinates only for the C₁, O₁, O₂, and H₁ are different between the A and B configurations, the summation over i was limited only to these atoms. The potential $V_1(r_{ij})$ and $V_2(r_{ij})$ comes close to zero at large values of r_{ij} . Consequently, a summation limit is generally imposed on the distance r_{ij} .²⁰⁾ In this case, the summation limit was placed at 6 Å. For $V_2(r_{ij})$, the summation was made to include the atom j of the molecules in 26 neighboring unit cells. Most of the numerical calculations were performed by a Facom

230-75 computer at the Data Processing Center, Kyoto University. Some calculation were made by a Facom 230-48 computer of this institute.

RESULTS AND DISCUSSIONS

Table IV shows the energy difference between the *A* and *B* crystal structures calculated by using Eqs. (4) to (6). In this table, the contributions of $V_1(r_{ij})$ and $V_2(r_{ij})$ to ΔH_{inter} are separately shown. The Coulombic potential $V_2(r_{ij})$ does not contribute to ΔH_{intra} , since the atoms with residual charges in the *B* configuration are at the mirror images of the corresponding ones in the *A* configuration.

It is found from Table IV that ΔH_{total} is negative irrespective of the potential parameter used. This shows that the *A* crystal structure is more stable than the *B* crystal structure. Consequently, the configuration at 0°K is assigned to the *A* configuration, in accord with the assignment made previously.¹⁾ Both the intermolecular part ΔH_{inter} and the intramolecular part ΔH_{intra} have negative values except only for ΔH_{intra} of Parameter Set II. The intermolecular part ΔH_{inter} comes mainly from the Coulombic energy term $\Delta H_{\text{inter}}[V_2]$. The Coulombic interaction, that is, the intermolecular interaction among polar groups, play an important role in generation of the enthalpy difference between the *A* and *B* crystal structures.

Now let us discuss the physical meaning of the intramolecular part ΔH_{intra} . If the dimer molecule in the *A* configuration is isolated and undergoes the simultaneous proton transfer, it may be transformed into the energetically and geometrically equivalent molecule.^{4,5)} In the molecular model of the *A* configuration in Fig. 1, the $\overline{C_1C_2}$ and $\overline{C_1'C_2'}$ are not co-linear. Consequently, when the simultaneous proton transfer occurs in the isolated dimer, not only the H_1 and H_1' protons but also the C_1 and C_1' atoms and the benzene rings could not keep the original positions in order to produce the isolated *B* configuration which is energetically and geometrically equivalent to the *A* configuration. In the crystal, however, the benzene rings may not easily move with the proton transfer, being hindered by the crystal packing forces. This is the reason why ΔH_{intra} occurs.

The calculated energy difference ΔH_{total} between the two crystal structures, *A* and *B*, does not directly correspond to the observed value ΔH_{obs} . Because, the observed value ΔH_{obs} between the two molecular configurations is obtained for the crystal which contains randomly the *A* and *B* configurations at the approximate C_i sites,³⁾ while the calculated one is obtained for the pure *A* and *B* crystals. If we consider this, the calculated values

Table IV. Calculated Enthalpy Difference between the *A* and *B* Crystal Structures (in kcal/mol)^{a)}

Parameter set	ΔH_{intra}	$\Delta H_{\text{inter}} [V_1]^b)$	$\Delta H_{\text{inter}} [V_2]^c)$	ΔH_{inter}	ΔH_{total}
I	-0.14	0.02	-0.24	-0.22	-0.36
II	0.03	0.03	-0.24	-0.21	-0.18
III	-0.19	0.00	-0.24	-0.24	-0.43
IV	-0.12	0.11	-0.24	-0.13	-0.25

a) Observed value is about -0.1 kcal/mol (not correspond exactly to ΔH_{total} ; see the text).

b) Terms due to $V_1(ij)$ (potential energy for neutral atoms).

c) Terms due to $V_2(ij)$ (Coulombic energy).

ΔH_{total} 's of about -0.2 to -0.4 kcal/mol seem to be reasonable as compared with the observed value ΔH_{obs} of about -0.1 kcal/mol.

CONCLUSION

The present calculation indicates that the *A* configuration in crystalline benzoic acid is more stable than the *B* configuration which may be produced from the *A* configuration by the simultaneous proton transfer along the two hydrogen bonds of a dimer. The crystal structure (or molecular configuration) at 0°K is assigned to the *A* crystal structure (or the *A* configuration). The calculation gives the reasonable energy difference between the *A* and *B* crystal structures. The calculation also shows that the Coulombic interaction energy plays an important role in generation of the energy difference between the two crystal structures.

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